Enzyme-Mediated Surface Modification of Jute and its Influence on the Properties of Jute/Epoxy Composites

Xiaoyan Ni,[1] Aixue Dong,[1] Xuerong Fan,[1,2] Qiang Wang,[1,2] Yuanyuan Yu,[1] Artur Cavaco-Paulo[2,3]
[1]*Key Laboratory of Science and Technology of Eco-Textile, Ministry of Education, Jiangnan University, Wuxi, 214122 Jiangsu, China*

[2]*International Joint Research Laboratory for Textile and Fiber Bioprocesses, Jiangnan University, Wuxi, 214122 Jiangsu, China*

[3]*Department of Biological Engineering, University of Minho, 4710-057 Braga, Portugal*

Surface modification of jute fibers is necessary to improve the adhesion and interfacial compatibility between fibers and resin matrix before using fibers in polymer composites. In this study, dodecyl gallate (DG) was enzymatically grafted onto the jute fiber by laccase to endow the fiber with hydrophobicity. A hand lay-up technique was then adopted to prepare jute/epoxy composites. Contact angle and wetting time measurements showed that the surface hydrophobicity of the jute fabric was increased after the enzymatic graft modification. The water absorption and thickness swelling of the DG-grafted jute fabric/epoxy composite were lower than those of the other composites. The tensile and dynamic mechanical properties of the jute/epoxy composites were enhanced by the surface modification. Scanning electron microscopy images revealed stronger fiber–matrix adhesion in composites with modified fibers. Therefore, the enzymatic graft modification increased the fiber–matrix interface area. The fiber–matrix adhesion was enhanced, and the mechanical properties of the composites were improved. POLYM. COMPOS., 00:000–000, 2015.

INTRODUCTION

With increasing awareness of ecological and environmental issues, the desire to obtain products from renewable materials has triggered an increased interest in natural plant fibers such as jute, sisal, flax, kenaf, and hemp. Natural fiber reinforced composites have been widely used in many applications because of their recyclability, renewability, low density, low cost, low toxicity, ease of separation, and excellent specific mechanical properties compared with traditional materials [1–4]. However, the application of natural fibers in composites also has some drawbacks, including poor compatibility toward a hydrophobic polymer matrix and moisture absorption causing plasticization and swelling effects, resulting in weak interfaces and poor mechanical properties of the composites [5, 6].

Therefore, pretreatments of natural fibers aimed at improving the adhesion between fibers and matrix are necessary before using them in polymer composites. A number of methods have been studied to enhance the compatibility of the fiber surface to the matrix, including alkali treatment [7, 8], silane treatment [9], plasma treatment [10, 11], UV irradiation [12], ionizing radiation [13], graft copolymerization [14], isocyanate treatment [15], and their combination treatments [16]. In surface modification, either fiber surface structure is changed or new compounds were incorporated onto the surface of the fiber that can effectively interlock with the matrix. Nevertheless, these pretreatments also have some disadvantages, such as high demands for the process, serious fiber damage in physical means, and homopolymerization of the monomers in chemical grafting, which would decrease the grafting efficiency and cause the waste of the monomers.

Enzymatic treatment of fibers is a new environmentally friendly method that is applied prior to composite production to obtain a good fiber–matrix interfacial bonding [17, 18]. The enzymatic reactions are specific and have a focused performance, which could be cost effective and improve product quality. Laccase (EC 1.10.3.2), as a kind of multicopper oxidase, can catalyze the

Correspondence to: Qiang Wang; e-mail: qiang_wang@163.com
Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 51173071; contract grant sponsor: Program for New Century Excellent Talents in University; contract grant number: NCET-12-0883; contract grant sponsor: Fundamental Research Funds for the Central Universities; contract grant sponsor: JUSRP51312B.
DOI 10.1002/pc.23699
Published online in Wiley Online Library (wileyonlinelibrary.com).

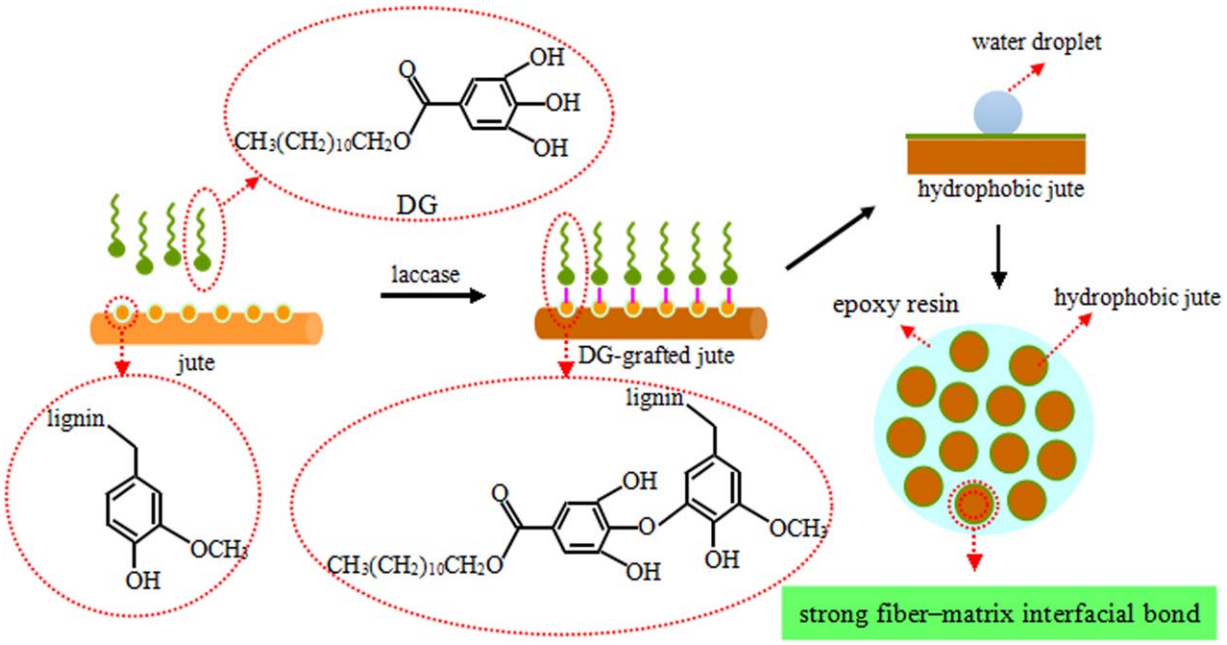

FIG. 1. Schematic illustration of laccase-catalyzed grafting reaction of DG onto the jute fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monoeletronic oxidation of phenols and aromatic or aliphatic amines to reactive radicals in a redox reaction [19]. Lignin in lignocellulosic fibers is a suitable substrate for laccase. The phenolic sites of lignin can be oxidized to phenoxyl radicals by laccase, and the reactive radicals could initiate the grafting of foreign functional molecules to produce new engineering materials [20, 21]. Among the lignocellulosic fibers, jute fiber has appeared to be one of the most promising candidates used for biocomposites because of its low specific gravity, high specific modulus, and low cost [22]. Epoxy polymers are considered to be one of the most important classes of thermosetting polymers due to their outstanding mechanical and thermal properties [23, 24]. Much attention has been given to improve the interfacial bonding between jute fiber and epoxy matrix, and results indicated that surface treatments of jute fibers such as alkali, silane, and acrylic acid could significantly improve the mechanical properties of the jute/epoxy composites [25, 26].

In our previous work [27], dodecyl gallate (DG) was enzymatically grafted onto jute fabric by laccase to increase the surface hydrophobicity of the fiber. The schematic illustration of the reaction is presented in Fig. 1. In this study, the enzymatic grafting of DG onto jute fibers provided a new approach for the modification of the fiber reinforced materials in composites, and the effects of enzymatic surface treatments on the jute fiber surface and jute/epoxy interface were investigated. The jute/epoxy composites were fabricated by hand lay-up process. The hydrophobicity of the jute fiber surface was characterized by contact angle and wetting time. The reinforcement mechanism of hydrophobic jute fabrics for epoxy composites was studied by scanning electron microscopy (SEM), tensile tests, and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

Raw jute fabric (100%) with a 7/7 (warp/weft) cm^{-1} yarn count was supplied by Longtai weaving (Changshu, China). Laccase (Denilite II) with an activity of 45 U/g from *Aspergillus* was provided by Novozymes (Shanghai, China). One unit of laccase activity is defined as the amount of enzyme which oxidizes 1 μmol of 2,2-azino-bis-3-ethyl-benzo-thiazoline-6-sulfonic acid per minute under specific reaction conditions. DG (98% purity) was obtained from J&K Technology (Beijing, China). Epoxy E 51 (bisphenol A) and epoxy hardener 9055 (isocyanic acid) obtained from Lanxing Chemical New Materials (Wuxi, China) were used in this study. All other reagents were purchased in China and were of analytical grade.

Pretreatment of Jute Fabrics

The jute fabrics were Soxhlet-extracted with a 2:1 mixture of benzene and ethanol at 90°C for 12 h to remove lipophilic extractives, followed by boiling with distilled water for 3 h. As a result, more lignins were exposed on the surfaces of the jute fibers.

Enzymatic Grafting of DG onto Jute Fibers

Jute fabrics were preoxidized by laccase (2.5 U/ml) for 10 min and then incubated for 4 h in the presence of DG

 DOI 10.1002/pc

(10 mM) in a shaking bath. The reaction was allowed to proceed in 80/20 (v/v%) of 0.2 M acetate buffer/EtOH solutions with a fabric-to-liquor ratio of 1:50 at pH 3.5 and 50°C. After the reaction, the jute fabrics were first rinsed with deionized water at 80°C for 20 min, then washed with water, and then air-dried. Finally, the jute fabrics were Soxhlet-extracted with acetone at 75°C for 12 h. Each experiment was performed in triplicate.

Fabrication of Composite

A hand lay-up technique was used to prepare composite samples. The working surfaces were treated with silicone spray to facilitate easy removal of moulds. To make the epoxy matrix, the epoxy resin and hardener were mixed in a mass ratio of 2:1. Subsequently, 25 wt% of acetone (as diluents) was added, and the mixture was stirred by a mechanical stirrer for 10 min. The epoxy matrix was applied to the jute fabrics using a smooth brush. A roller was used to achieve uniform distribution of epoxy matrix throughout the layer surface. Prepregs were allowed to dry in air at room temperature for 12 h. Then, two prepregs were placed one over the other in the mould under a pressure of 4 MPa and at 115°C by using hot pressing for 2 h. The composites were then removed from the mold and cured at room temperature for further use. The composite samples were prepared in such a manner that the expected fiber loading would be around 40 wt%.

Contact Angle Measurements

After conditioning the jute fabric samples to equilibrium moisture content, the contact angle of water was measured using a SL200B static contact angle/interfacial tension meter (Kino Industry). The volume of each droplet was 2 μl. For each sample, the contact angle was measured on five spots, and the results were averaged.

Dimension Stability Test

The water absorption and thickness swelling were determined in accordance with ASTM D 5229. Before testing, the weight and thickness of each composite sample (100 mm × 20 mm × 1 mm) were measured. Each type of composite samples was immersed in distilled water at room temperature for 24 h and then taken out and wiped with filter paper to remove surface water before measurement of weight and thickness. The samples were reimmersed in water to continue sorption until saturation. The dimension stability test continued for several days until constant weight of a sample was attained.

Thermogravimetric Analysis Measurements

Thermogravimetric analysis (TGA) test of the jute fibers was performed using a TGA/SDTA 851e thermogravimetric analyzer (METTLER TOLEDO, Switzerland). Approximately 5 mg of sample was used in each test. The sample was heated from ambient to 700°C at a temperature ramp of 20°C/min[1] under nitrogen atmosphere.

Tensile Test

The tensile properties of jute/epoxy composites were determined using a KD111-5 microcomputer-controlled electronic universal testing machine as per the ASTM D 3039 specification. The samples with a dimension of 100 mm (length) × 20 mm (width) × 1 mm (thick) were fixed on the shelf of the universal testing machine. The gauge length was set at 60 mm, and the testing speed was 2 mm/min. A stress–strain curve of the composite and the data of the tensile strength and modulus were recorded. Five specimens for each configuration were tested and averaged.

Fracture Surface Analysis

The fracture surfaces of the jute-reinforced composites were investigated using a SU1510 SEM (Hitachi, Japan) under 5.00 kV at 3.00k magnification. All specimens were sputter coated with gold prior to examination.

DMA

A DMAQ800 analyzer (TA Instrument) was used for the evaluation of storage modulus (E'), loss modulus (E''), and damping parameter (tan δ). A three-point bending mode was used. The samples were tested in a fixed frequency of 1.0 Hz and a heating rate of 5°C/min. The samples were evaluated in the range from 30°C to 120°C. Each sample has a thickness of 1.5 mm, a width of 8 mm, and a length of 60 mm.

RESULTS AND DISCUSSION

Hydrophobicity of Jute Surface

To study the surface properties of jute used for the fabrication of jute/epoxy composites, the static water contact angles of jute fabrics were measured. The wettability of fibers can indicate their hydrophilicity or hydrophobicity, which is an important factor for the adhesion and interfacial compatibility with the hydrophobic epoxy matrix. The time-dependent contact angle of a water drop on jute fabric samples is shown in Fig. 2.

The untreated jute fabrics were hydrophilic in nature showing contact angle values of 106.61°, and the water droplet disappeared within 5 s. The contact angle of the laccase-treated jute fabric was increased to 118.13°, and the water droplet disappeared after 15 s. The enhanced hydrophobicity of the laccase-treated jute fabrics was possibly due to the enzymatic oxidation and polymerization of lignin on the jute surface [27]. The jute fabric modified

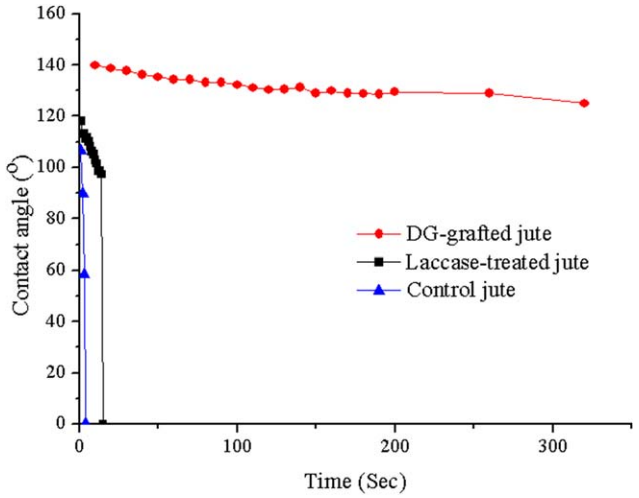

FIG. 2. Contact angles over time for the control, laccase-treated jutes, and DG-grafted jutes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

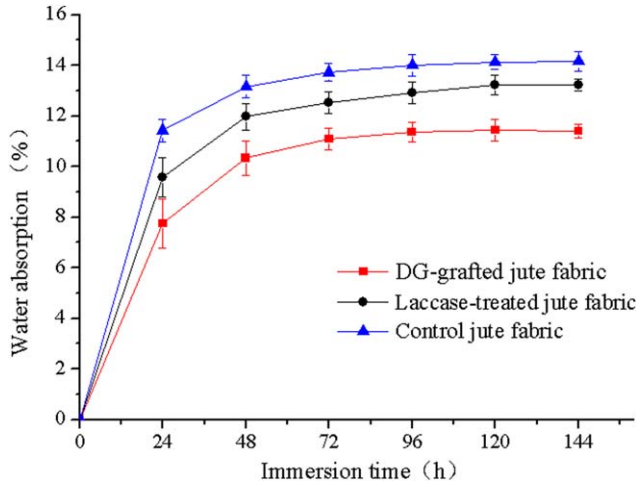

FIG. 3. Percentage weight gained by the composites in water as a function of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with DG showed a contact angle of 139.87°, which decreased to 128.97° after 300 s, indicating a better hydrophobicity. The increased contact angle and wetting time indicated that the surface hydrophobicity of the jute fabric was increased after graft modification with DG, which showed a more significant improvement of hydrophobicity on the jute than the combined treatment of alkaline and silane coupling agent [25]. The enhanced hydrophobicity can be mainly due to the presence of DG, which contains a long hydrocarbon chain on the surface of the jute fabric.

Water Absorption and Thickness Swelling of Composites

The hydrophilic properties of jute fibers and the capillary action facilitate the intake of water when the composite samples were immersed in water, resulting in increased dimension of the composite. To improve the interfacial adhesion and stability of the composites, understanding of the water absorption process and the impact of the absorbed water on the dimensional change is important [28].

The weight change gained by the composites in water as a function of time is shown in Fig. 3. The result showed that the weight percentage gained by each composite increased rapidly in the initial stage, and then the absorption became slower and static when equilibrium was established in water. It was observed that the water absorption for the DG-grafted jute fabric/epoxy composite (11.43%) was the lowest among the different types of composite. By contrast, the control jute fabric-reinforced composite presented the highest water absorption (14.18%). As shown in Fig. 4, the thickness swelling of the control jute fabric/epoxy composite (17.84%) was the highest among the different types of composite. By contrast, the dimensional stability for the DG-grafted jute fabric/epoxy composite (12.62%) was the lowest. The laccase-treated jute fabric/epoxy composite showed a moderate dimensional stability with moderate thickness swelling (16.52%).

The water absorption behavior and dimensional stability of the composites with the natural fibers are important properties that could have deleterious effects on mechanical and physical properties [29]. Higher moisture content of the jute fiber leads to poor wettability with epoxy resin, thereby weakening the interfacial bonding between the fiber and epoxy matrix [30]. As several long hydrocarbon chains of DGs have been grafted onto the surface of the jute fibers, the surface hydrophobicity of the jute fiber has improved the surface adhesion between fibers and matrix, thereby reducing the water accumulation in the interfacial voids [31].

TGA Analysis

TGA analysis was used to investigate the decomposition patterns and thermal stability of the jute fibers. The TGA

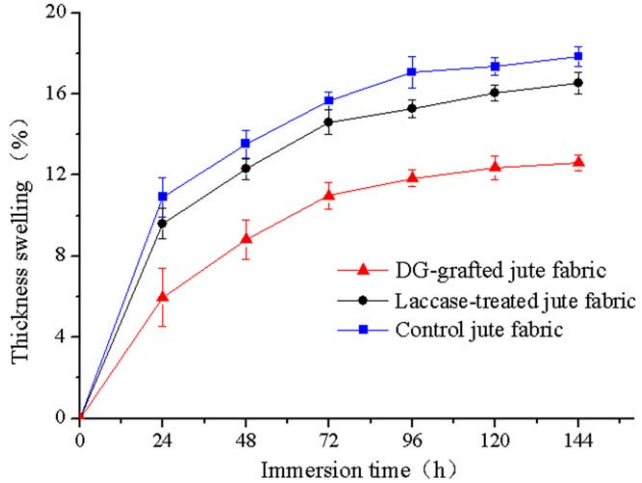

FIG. 4. Thickness swelling of the composite in water as a function of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DOI 10.1002/pc

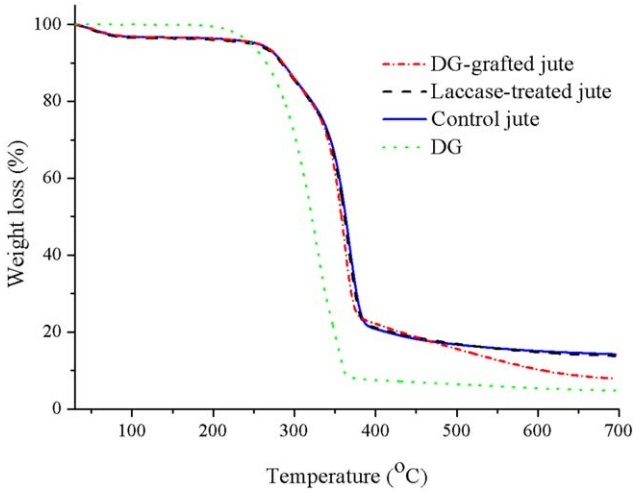

FIG. 5. The TGA curves of the jute fabric samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and derivative of thermograms (DTG) curves of the jute fabric samples are shown in Figs. 5 and 6. In the case of the DG, a major decomposition occurred from 200°C to 370°C, and the pyrolysis of the main components in DG occurred at about 327°C. For the jute fibers, after initial loss of moisture and desorption of gases below 100°C, a major decomposition occurred from 250°C to 390°C. The DG-grafted jute got the maximum mass loss rate at 361°C, representing a decrease of 6°C when compared with those of the control and laccase-treated jute (367°C). It is obvious that no degradation occurred until 200°C. Since the jute/epoxy composites were prepared at 115°C by using hot pressing, the hydrocarbon chains on the surface of the DG-grafted jute fabric would not be damaged.

Tensile Properties

The mechanical properties of fiber-reinforced composites depend not only on the properties of the constituents

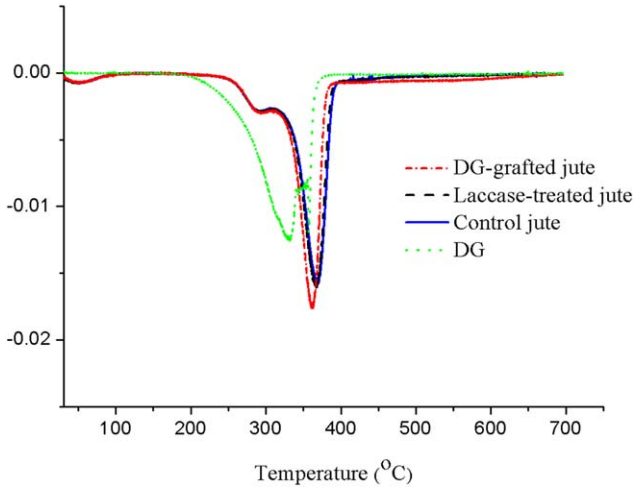

FIG. 6. The DTG curves of the jute fabric samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 1. Tensile properties of the different composites.

Composites	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
Control jute/epoxy	36.52 ± 1.95	0.82 ± 0.15	9.23 ± 0.05
Laccase-treated jute/epoxy	37.36 ± 1.44	1.14 ± 0.19	8.20 ± 0.01
DG-grafted jute/epoxy	50.30 ± 0.36	1.41 ± 0.13	7.56 ± 0.23

but also on the degree of interfacial adhesion between the fiber and the matrix. A strong fiber–matrix interfacial bond is significant for high mechanical properties and effective stress transfer from the matrix to the fiber whereby maximum utilization of the fiber strength in the composite [32]. The tensile properties were investigated to observe the effect of jute fabric surface modification on the compatibility between the jute fabric and epoxy matrix.

Results of the tensile properties (tensile strength, tensile modulus, and elongation at break) of different composites are summarized in Table 1. The DG-grafted jute fabric-reinforced composites presented the highest tensile strength (50.30 MPa), followed by the laccase-treated jute/epoxy composite (37.36 MPa) and the control jute/epoxy (36.52MPa) composites in order. It is evident that the graft modification of the jute fabrics remarkably increased the tensile modulus of the composites. The composites prepared using the DG-grafted jute showed considerable enhancement in tensile strength and tensile modulus, with an increase of 37% and 72%, respectively, with respect to those of the untreated jute reinforced composites. The elongation at break of DG-grafted jute fabric-reinforced composites (7.56%) was less than the composites reinforced with laccase-treated fabric (8.20%) and untreated fabric (9.23%). The stress–strain curves of different jute/epoxy composites are plotted to determine their ultimate tensile

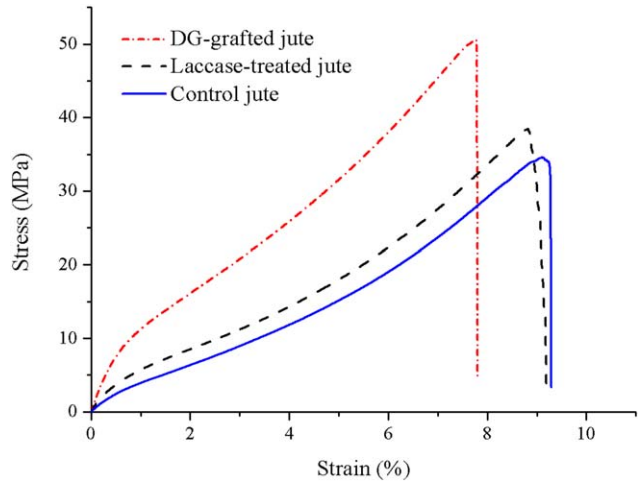

FIG. 7. Stress–strain curve of different composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

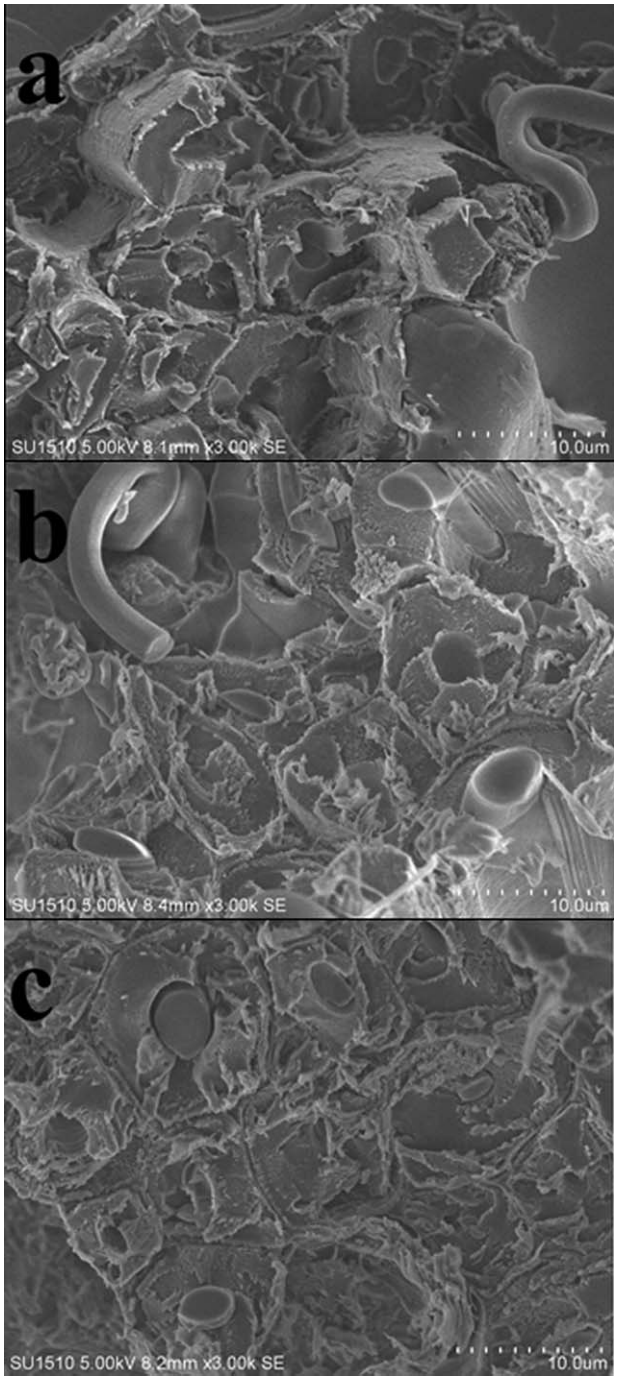

FIG. 8. SEM images of the fracture sections of epoxy composites reinforced by (a) control jute fabric, (b) laccase-treated jute fabric, and (c) DG-grafted jute fabric.

strength and elastic modulus (Fig. 7). The curves indicated that graft modification of the jute fabric endowed it with a higher strength but lower ductility. A previously published study by Michael et al. reported that silane surface treatment had a significant effect on tensile modulus (36% increase) but no significant effect on the tensile strength of the jute/epoxy composites [26].

The increase in tensile strength and modulus of the DG-grafted jute fabric-reinforced composites may be due

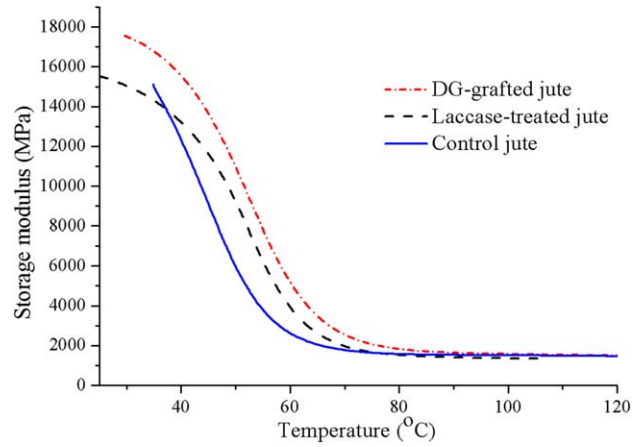

FIG. 9. Storage modulus of the epoxy resin composites reinforced with DG-grafted, laccase-treated, and control jute fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the improved adhesion between the jute fiber and the epoxy matrix. This improved adhesion might have enhanced the interfacial bonding and thus made it easier for the stress to be effectively transferred from the matrix to the fiber.

Fracture Surface Analysis

The SEM micrographs of the surfaces of tensile fractured specimens are shown in Fig. 8. For the control jute fabric/epoxy composite (Fig. 8a), a considerable degree of fiber–matrix debonding and numerous cracks and fiber pullout were observed. These observations indicated poor interfacial adhesion, which is probably due to a large difference in the surface energies between the fibers and the matrix [33]. The composites of the jute fabric treated with laccase (Fig. 8b) also showed rough and irregular in fracture section. On the contrary, DG-grafted jute fabric/epoxy composite (Fig. 8c) showed relatively higher fiber–

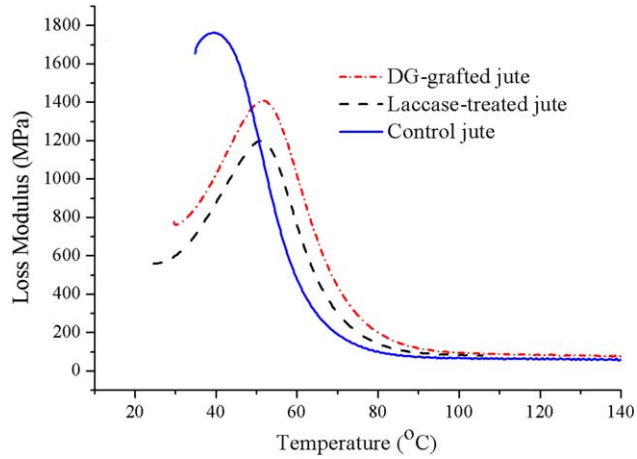

FIG. 10. Loss modulus of the epoxy resin composites reinforced with DG-grafted, laccase-treated, and control jute fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DOI 10.1002/pc

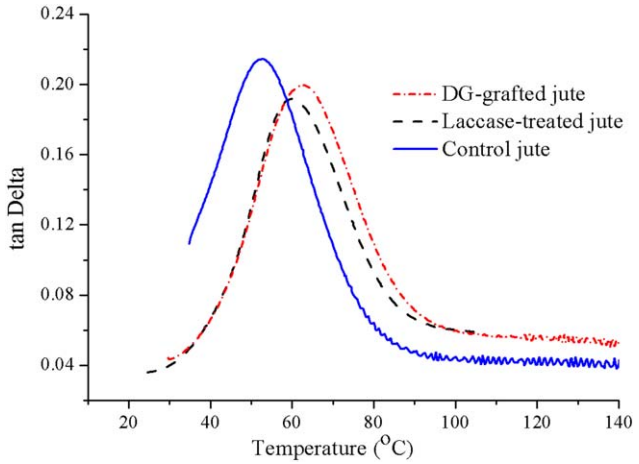

FIG. 11. Normalized tan δ of the epoxy resin composites reinforced with DG-grafted, laccase-treated, and control jute fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matrix adhesion. The fibers were bonded to the matrix, thereby ensuring adequate load transfer to the matrix; as a result, the fibers break flush with the matrix during tensile fracture. The enhanced interfacial compatibility could be attributed to the surface hydrophobization of the jute fabric, which satisfies the requirement for reinforcing the composites of the better mechanical properties. Therefore, graft modification has improved the fiber–matrix adhesion of jute/epoxy composites.

DMA Analysis

The DMA results of jute/epoxy composites can be used to determine the interfacial properties between the jute fiber and epoxy matrix. The E', E'', and normalized tan δ curves of the composite samples are illustrated in Figs. 9–11.

The E' versus temperature curve provides valuable information about stiffness, degree of crosslinking, and fiber/matrix interfacial bonding of materials [34]. The E' values decreased with the increase in temperature, and then a sharp decline in the E' value was observed at the glass transition region because of the molecular mobility of the polymer chains above the glass transition temperature (T_g). Figure 9 shows a notable increase in the modulus of epoxy composites reinforced with DG-grafted jute fabrics. This increase might be attributed to the improved interfacial adhesion between the fibers and the matrix, which allowed a greater degree of stress transfer at the interface.

TABLE 2. Peak height, tan δ_{max} (T_g), and E''_{max} (T_g) of jute/epoxy composites.

Composite samples	Peak height of tan δ curve	T_g from tan δ_{max} (°C)	T_g from E''_{max} (°C)
Control jute/epoxy	0.21	52.65	39.35
Laccase-treated jute/epoxy	0.19	59.95	51.19
DG-grafted jute/epoxy	0.20	62.49	51.51

Figure 10 shows the change in E'' of the jute/epoxy composites with temperature. E'' is a measure of energy dissipated as heat/cycle under deformation or it is viscous response of the materials [35]. The maximum E'' occurred at the temperature where E'' was maximum, indicating the T_g of the system. The T_g values obtained from the E'' curves are shown in Table 2. T_g shifted to higher temperatures with the increase in hydrophobicity of the jute fabrics. This shift was primarily attributed to the segmental immobilization of the matrix chain at the fiber surface [36]. The T_g values obtained from E'' curves were found to be lower and more realistic than that obtained from tan δ curves [37].

The ration of E'' to E' is measured as the mechanical loss factor or tan δ. The tan δ values of the jute/epoxy composites are shown in Fig. 11, in which tan δ increased with increasing temperature, reached maximum in transition region, and then decreased in rubbery region. The damping peak in the DG-grafted jute fabric/epoxy composites showed a decreased magnitude of tan δ compared with the control jute fabric/epoxy composites. The results indicated that the DG-grafted jute fabric/epoxy composites with strong interfacial bonding between the fibers and epoxy matrix would carry a greater extend of stress and allow only a small part of it to strain the interface [38].

Recently, researchers reported on dynamic mechanical properties of epoxy hybrid composites fabricated by reinforcing 2-hydroxy ethyl acrylate treated jute and oil palm empty fruit bunch fibers [3]. Results indicated that chemical modification of natural fibers could enhance thermal properties of hybrid composites. In this work, DMA data showed that the DG-grafted jute/epoxy composites had relatively high E' and T_g and relatively low tan δ values. The results revealed constriction effects on molecular mobility of matrix on the fiber surface, which is evidence of better interfacial bonding and well with the above-mentioned mechanical properties.

CONCLUSIONS

In this study, a hydrophobic modification approach via laccase-mediated grafting was developed for jute fabrics. The contact angle (139.87°) and wetting time (more than 30 min) revealed that the enzymatic graft modification endowed the jute fibers with hydrophobicity. TGA results showed that the hydrocarbon chains on the surface of the DG-grafted jute fabric would not be damaged during hot pressing. The decrease in water absorption and thickness swelling of the DG-grafted jute fabric/epoxy composite indicated that the composite possessed better water repellency and dimensional stability after graft modification. For the modified jute/epoxy composites, both the tensile strength and modulus were increased, and fiber breakage

in fracture surface showed effective stress transfer between fibers and matrix. The higher E' value, a shift in E'' to a higher temperature, and lower tan δ peak height of the DG-grafted jute fabric/epoxy composite indicated that the adhesion between jute fibers and matrix was increased after graft modification of jute. Therefore, DG, having a molecular structure composed of a hydrophobic alkyl chain, was introduced into jute fibers to prepare a novel jute/epoxy composite which has excellent tensile and dynamic mechanical properties. It is likely that enzyme-mediated hydrophobic modification of jute can be considered as an effective and environmentally friendly method for enhancing the reinforcement efficiency of jute fibers and the properties of jute/epoxy composites.

REFERENCES

1. H. Deveci, *Polym. Compos.*, **34**(8), 1375 (2013).
2. S.H. Bhosale, V.V. Singh, M.C. Rangasai, S. Bandyopadhyay-Ghosh, and S.B. Ghosh, *Polym. Compos.* (in press); DOI 10.1002/pc.23192.
3. M. Jawaid, O.Y. Alothman, N. Saba, M.T. Paridah, and H.P.S. Abdul Khalil, *Polym. Compos.* (in press); DOI 10.1002/pc.230772014.
4. R. Yahaya, S.M. Sapuan, M. Jawaid, Z. Leman, and E.S. Zainudin, *J. Reinf. Plast. Comp.*, **33**(24), 2242 (2014).
5. A. Arbelaiz, B. Fernández, Valea A, and I. Mondragon, *Carbohydr. Polym.*, **64**(2), 224 (2006).
6. L.Y. Mwaikambo and M.P. Ansell, *J. Appl. Polym. Sci.*, **84**(12), 2222 (2002).
7. I. Van de Weyenberg, T.C. Truong, B. Vangrimde, and I. Verpoest, *Compos. Part A: Appl. Sci. Manuf.*, **37**, 1368 (2006).
8. E.T.N. Bisanda, *Appl. Compos. Mater.*, **7**(5–6), 331 (2000).
9. P.J. Herrera-Franco and A. Valadez-Gonzalez, *Compos. Part A: Appl. Sci. Manuf.*, **35**(3), 339 (2004).
10. X. Yuan, K. Jayaraman, and D. Bhattacharyya, *J. Adhes. Sci. Technol.*, **18**(9), 1027 (2004).
11. X. Xu, Y. Wang, X. Zhang, G. Jing, D. Yu, and S. Wang, *Surf. Interface Anal.*, **38**(8), 1211 (2006).
12. M.Z. Abedin, M.D.H. Beg, K.L. Pickering, and M.A. Khan, *J. Reinf. Plast. Comp.*, **25**(6), 575 (2006).
13. H.U. Zaman, M.A. Khan, and R.A. Khan, *Polym. Compos.*, **33**(7), 1077 (2012).
14. G. Cantero, A. Arbelaiz, R. Llano-Ponte, and I. Mondragon, *Compos. Sci. Technol.*, **63**, 1247 (2003).
15. M.S. Sreekala, M.G. Kumaran, S. Joseph, M. Jacob, and S. Thomas, *Appl. Compos. Mater.*, **7**(5–6), 295 (2000).
16. S.J. Eichhorn, C.A. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, K.M. Entwistle, P.J. Herrera-Franco, G.C. Escamilla, L. Groom, M. Hughes, C. Hill, T.G. Rials, and P.M. Wild, *J. Mater. Sci.*, **36**, 2107 (2001).
17. T. Stuart, Q. Liu, M. Hughes, R.D. McCall, H.S.S. Sharma, and A. Norton, *Compos. Part A: Appl. Sci. Manuf.*, **37**(3), 393 (2006).
18. C. Vigneswaran and J. Jayapriya, *J. Text. Inst.*, **101**(6), 506 (2010).
19. S. Riva, *Trends Biotechnol.*, **24**, 219 (2006).
20. D. Areskogh, J. Li, G. Gellerstedt, and G. Henriksson, *Biomacromolecules*, **11**(4), 904 (2010).
21. M. Lund and A. Ragauskas, *Appl. Microbiol. Biotechnol.*, **55**(6), 699 (2001).
22. A.K. Bledzki and J. Gassan, *Prog. Polym. Sci.*, **24**(2), 221 (1999).
23. R. Pearson and A. Yee, *J. Mater. Sci.*, **24**, 2571 (1989).
24. R. Konnola, J. Parameswaranpillai, and K. Joseph, *Polym. Compos.* (in press); DOI 10.1002/pc.23390.
25. T.T.L. Doan, H. Brodowsky, and E. Mäder, *Compos. Sci. Technol.*, **72**(10), 1160 (2012).
26. M.A. Pinto, V.B. Chalivendra, Y.K. Kim, and A.F. Lewis, *Polym. Compos.*, **35**(2), 310 (2014).
27. A. Dong, Y. Yu, J. Yuan, Q. Wang, and X. Fan, *Appl. Surf. Sci.*, **301**, 418 (2014).
28. Q. Lin, X. Zhou, and G. Dai, *J. Appl. Polym. Sci.*, **85**(14), 2824 (2002).
29. B. Mohebby, H. Younesi, A. Ghotbifar, and S. Kazemi-Najafi, *J. Reinf. Plast. Comp.*, **29**(6), 830 (2009).
30. M. Jawaid, H.A. Khalil, P.N. Khanam, and A.A Bakar, *J. Polym. Environ.*, **19**(1), 106 (2011).
31. M.M. Thwe and K. Liao, *Compos. Sci. Technol.*, **63**(3–4), 375 (2003).
32. R. Karnani, M. Krishnan, and R. Narayan, *Polym. Eng. Sci.*, **37**(2), 476 (1997).
33. S. Mohanty, S.K. Verma, and S.K. Nayak. *Compos. Sci. Technol.*, **66**(3), 538 (2006).
34. S. Joseph, S.P. Appukuttan, J.M. Kenny, D. Puglia, S. Thomas, and K. Joseph, *J. Appl. Polym. Sci.*, **117**(3), 1298 (2010).
35. N. Hameed, P.A. Sreekumar, B. Francis, W. Yang, and S. Thomas, *Compos. Part A: Appl. Sci. Manuf.*, **38**(12), 2422 (2007).
36. P.V. Joseph, G. Mathew, K. Joseph, G. Groeninckx, and S. Thomas, *Compos. Part A: Appl. Sci. Manuf.*, **34**(3), 275 (2003).
37. M. Akay, *Compos. Sci. Technol.*, **47**(4), 419 (1993).
38. S. Mohanty, S.K. Verma, and S.K. Nayak, *Compos. Sci. Technol.*, **66**(3), 538 (2006).